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Incidental nutrient transfers: Assessing critical times in agricultural catchments using high-resolution data

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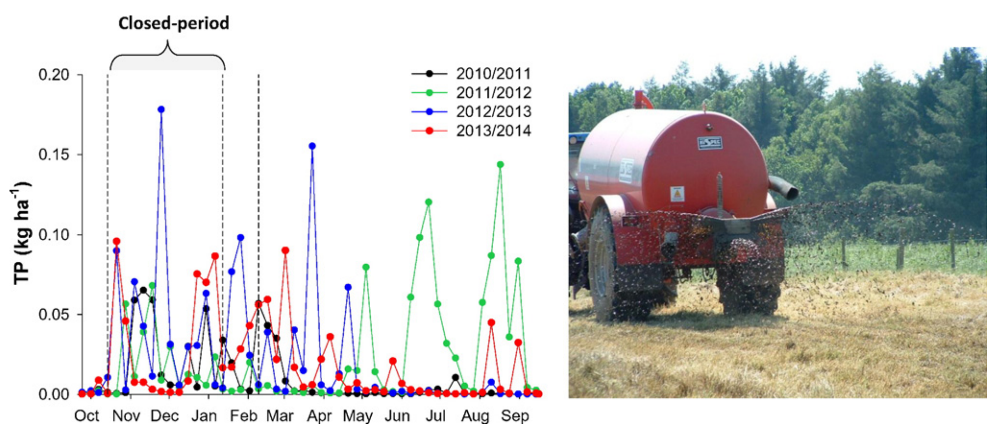
HIGHLIGHTS

- High resolution stream chemistry data were used to inform slurry application policy.
- 90th percentile storm discharges had signals of residual and incidental nutrient transfer.
- No incidental transfer signals were detected during the 4 weeks after the closed-period.
- There were indications of incidental transfers in a wet summer in two catchments.
- Regulations could be augmented with advice on soil moisture conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

Managing incidental losses associated with liquid slurry applications during closed periods has significant cost and policy implications and the environmental data required to review such a measure are difficult to capture due to storm dependencies. Over four years (2010–2014) in five intensive agricultural catchments, this study used high-resolution total and total reactive phosphorus (TP and TRP), total oxidised nitrogen (TON) and suspended sediment (SS) concentrations with river discharge data to investigate the magnitude and timing of nutrient losses. A large dataset of storm events (defined as 90th percentile discharges), and associated flow-weighted mean (FWM) nutrient concentrations and TP/SS ratios, was used to indicate when losses were indicative of residual or incidental nutrient transfers. The beginning of the slurry closed period was reflective of incidental and residual transfers with high storm FWM P (TP and TRP) concentrations, with some catchments also showing elevated storm TP:SS ratios. This pattern diminished at the end of the closed period in all catchments. Total oxidised N behaved similarly to P during storms in the poorly drained catchments and revealed a long lag time in other catchments. Low storm FWM P concentrations and TP:SS ratios during the weeks following the closed period suggests that nutrients either weren't applied during this time (best times chosen) or that they were applied to less risky areas (best places chosen). For other periods such as late autumn and during wet summers, where storm FWM P concentrations and TP:SS ratios were high, it is recommended that an augmentation of farmer knowledge of

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soil drainage characteristics with local and detailed current and forecast soil moisture conditions will help to strengthen existing regulatory frameworks to avoid storm driven incidental nutrient transfers.

1. Introduction

Transfers of nutrients such as nitrogen (N) and phosphorus (P) from agricultural land to water can pose a risk to receiving water-bodies resulting in eutrophication and water quality impairment (Seitzinger et al., 2010; Canfield et al., 2010). Diffuse nutrient transfers to water are mostly controlled by rainfall-runoff processes, with storm events responsible for delivering a large proportion of annual nutrient losses (Edwards and Withers, 2008). Diffuse transfers can also be approximately separated into those derived from soil nutrient stores that were not utilised by the crop, termed residual transfers, and those derived more directly from recently applied organic or inorganic fertilisers, termed incidental transfers (Preedy et al., 2001; Withers et al., 2003). Residual sources represent a potentially continuous nutrient pressure, which are only likely to become depleted in the medium to long-term (Schulte et al., 2010; Simpson et al., 2015). Recently applied nutrients can become incorporated into the soil profile, to become part of the residual store (Haygarth and Jarvis, 1999), as well as being an immediate potential incidental loss risk. In this regard, recently applied nutrients can be a transient source pressure.

As residual nutrient transfers tend to be continuous in nature and dependent on storm events, measures for managing these transfers have focussed on constraining the magnitude of nutrient applications to soils throughout the year, by restricting application rates based on, for example, soil P status (e.g. Ulén et al., 2007; Sims et al., 2000). Other constraints include the setting of maximum animal stocking rates to limit organic nutrient loading to the soil (e.g. OJEC, 1991). As incidental transfers are transient in nature, measures for management have focussed on restricting the timing of fertiliser and manure applications to when the risk of nutrient mobilisation is greatest; generally during the wetter winter periods when the soils have limited soil moisture deficits (SMD), and here termed the 'closed period'. Closed periods can vary in start/stop times and duration within and between countries depending on agri-environmental factors such as rainfall seasonality, amendment type (chemical fertilisers, slurries, farmyard manure, biosolids), soil drainage capacity and/or crop type (e.g. Wall et al., 2011; DEFRA, 2013; Swedish Board of Agriculture, 2009). Liquid slurries are a by-product in intensive cattle and pig enterprises and their closed periods are associated with costly storage facilities (Oenema et al., 2007) where the size of the facility is proportional to the storage period. Willingness to accept this particular measure can be problematic. For example, in a recent study of Irish farmers Buckley (2012) showed that a cohort to be sceptical about the validity of the slurry closed-period measure and believe it could actually increase the risk of diffuse pollution by concentrating slurry spreading at certain times in an effort to empty storage tanks.

The measures outlined above can be subject to periodic reviews, via a Driver-Pressure-State-Impact-Review (DPSIR) framework, following a monitoring and evaluation period (Murphy et al., 2015a). In the case of the slurry closed period measure, a review would require an evaluation of the critical times for slurry transfer to streams and with an emphasis on the potential for concentrated risk as identified by Buckley (2012). Whilst many reviews have been conducted using controlled studies at plot/field scales (Smith et al., 2003; Withers and Bailey, 2003; Sagoo et al., 2014), few have tried to link nutrient losses to 'normal' spreading activities at catchment scales where the integrated and net impact of these losses are revealed. Analysis of storm events (when incidental transfers are more likely to occur) at catchment scales is particularly poorly reported. There is a risk, therefore, of linking incidental nutrient transfer processes with non-storm (e.g. base flow) data and this might not be fully linked to cause and effect (e.g. Flynn et al., 2015). This dearth of catchment scale studies is likely due to the difficulties with collecting storm data, disaggregating the influence of slurry sources from others such as soil and point-source discharges, and other processes such as baseflow dilution, which serve to 'dampen' the slurry signals (Withers and Hodgkinson, 2009; Haygarth et al., 2012). Furthermore, slurry nutrient signals can be difficult to detect when only a small number of fields in a catchment receive slurry (Withers et al., 2003) and the need to capture data during storm events, when diffuse residual and incidental losses are occurring, requires a specific monitoring infrastructure (Sharpley et al., 2008). In specific storm events from plots in the UK, Withers and Bailey (2003) found that the proportion of total P exported in soluble reactive forms increased by 35% on plots which had received slurry, compared to control plots. Likewise, Bechmann and Vaje (2002) proposed that increased ratios of total P to suspended sediment (TP:SS) at the catchment scale in Norway was an indicative slurry signal during storm events. Ammonium (NH_4) follows a similar storm dependency as P from slurry amendments and elevated concentrations have been found during autumn and winter runoff events following applications (Turtola and Kemppainen, 1998). Ammonium in soil applied animal slurries can also be quickly converted to nitrate (NO_3), that can also be present as a surface runoff signal in subsequent storm events (Ceretta et al., 2010), or, more normally, a delayed groundwater signal (Ryan and Fanning, 1996; Di and Cameron, 2002; Kramers et al., 2012).

Whilst sophisticated techniques for detecting animal manures in flowing water are reported, such as genetic fingerprinting of bacteria associated with faecal matter (Gourmelon et al., 2007; Murphy et al., 2015b) and isolating nitrogen and carbon ratios (Jarde et al., 2007; Choi et al., 2007), these are emerging technologies, can be expensive, time-consuming (and not easily captured in storm events) and require a high level of technical expertise. In the absence of these tracers, identifying increased nutrient concentrations in similar storm discharges would provide an indication of elevated nutrient source pressures, which may have been due to (or at least indicate a sensitivity to) additional slurry applications, and thus would strengthen the review process. However, identifying increased nutrient concentrations in similar storm discharges is only possible with combinations of high-resolution nutrient chemistry and stream discharge. For this study, filtered fractions of P, NH_4 and the more sophisticated tracing techniques were only available through the analysis of discretely and infrequently captured samples during storm events. This limited the potential analysis due to the range and number of storms that could be sampled (Kotlash and Chessman, 1998). However, bankside sample and analysis equipment were also deployed to measure total reactive P (TRP, operationally equivalent to unfiltered molybdate-reactive P) and total digested P (TP), total oxidised N (TON = Nitrate-N + Nitrite-N (NO_2—N)) and suspended sediments with river discharge on a continuous basis and captured the full range of hydrological conditions, including storm events (Jordan et al., 2007; Outram et al., 2014).

Therefore, based on these principles, this study sought to examine a high resolution, four-year river water quality dataset in five meso-scale agricultural catchments subject to slurry closed period restrictions. The objectives were to:

1. Identify the timing of greatest nutrient loading downstream.
2. Identify signals of elevated nutrient source pressures, as detected in similar storm discharges at catchment outlets.
3. Identify when signals of increased nutrient source pressures were indicative of incidental slurry transfers.

This analysis was based on an interpretation of high-resolution water quality data resulting from 'normal' practices rather than controlled experiments (Ryan and Fanning, 1996; Sagoo et al., 2014) or a reliance on modelling approaches (Chambers et al., 1999). The analysis, therefore, provides a new insight into cause and effect patterns of storm induced residual and incidental nutrient transfers. Whilst organic nutrient fractions in storm discharges would have augmented this method, there is currently a technology gap for obtaining an accurate and continuous organic nutrient dataset. Nevertheless, grab sampled organic nutrient data were used to augment the high-resolution inorganic nutrient datasets.

For review purposes, these patterns were characterised according to their occurrence during storm events in the closed period, the adjacent 'shoulder periods' and the open period (i.e. the rest of the year). The 'shoulder periods' (i.e. periods of perceived increased risk – Buckley 2012) included the four weeks before the start of the closed period (termed the 'before' shoulder period) and the four weeks after the end of the closed period (termed the 'after' shoulder period).

1.1. Study areas

Data from five meso-scale (3.5 km^2 to 12.1 km^2) agricultural catchments in Ireland were used in this study (Figs. 1, S1). Three catchments are dominated by grassland (Grassland A, B, C) and two have high proportions of spring barley or winter wheat cropping (Arable A, B). The grassland land use ranges from relatively extensive beef to intensive dairying, and organic nutrient loadings vary widely (Table 1). The area, rainfall (measured as described in Section 2.2), geological characteristics and organic nutrient loadings of each catchment are shown in Table 1. The organic nutrient loadings were based on stock type and number, collated as catchment totals from farm records, and nutrient coefficients from published values used in the European Union (EU) Nitrates Directive (OJEC, 1991) regulations for Ireland (SI 31, 2014).

Based on their soil (Fig. S1) and geological characteristics and the soil drainage typologies of Schulte et al. (2005), Grassland A and Arable A, are characterised as free-draining, Arable B is characterised as moderately drained and Grassland B and Grassland C are characterised as poorly drained. Mellander et al. (2012) has provided detailed descriptions of the flow and nutrient transfer pathways during storm events in four of these catchments (all except Grassland C). In summary, in the two freely draining catchments, up to 96% of the hydrological pathways were below-ground, delivering up to 97% of the event flow TON load, and up to 63% of the event flow P load. In the two other catchments with poor to moderately drained soils, up to 55% of the hydrological pathways were quick flow, delivering up to 50% of the event flow TON load and up to 88% of the event flow P load.

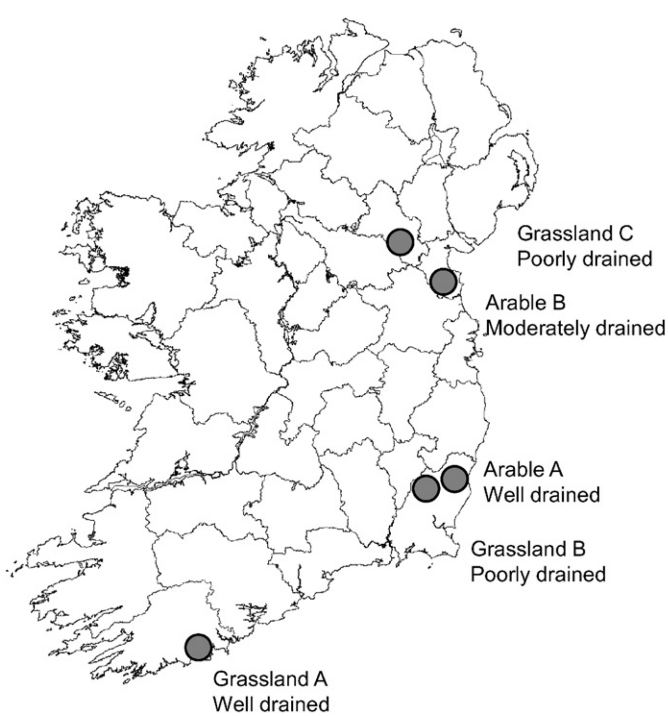

Fig. 1. Location of the five study catchments in Ireland. Further details are given in Table 1.

2. Methods

2.1. Closed period boundaries

In years with particularly adverse weather conditions, derogations to reduce the length of the closed period were sought and granted to alleviate the impacts of weather related difficulties (such as fodder shortage and the need for additional slurry storage) on farm management and profit margins. The 'regular' (2010/2011, 2013/2014) and derogated (2011/2012, 2012/2013) closed periods for slurry applications are shown in Table 1 and vary between catchments. In a pre-processing analysis, it was determined that no catchments had significantly higher (as measured using Mann-Whitney rank sum pairwise comparisons, Sigmaplot 11.0, $P > 0.05$) storm FWM P concentrations during a derogated period, compared to all corresponding non-derogated periods (data not shown). This finding justified focussing the analysis on the 'regular' closed period dates (Table 1), rather than on the modified dates, which allows consistency in the analysis and is more useful for informing reviews of the regular closed period.

2.2. Critical times for nutrient mobilisation

A meteorological-station (Campbell Scientific BWS-200) located near the centre of each catchment provided rainfall, wind-speed and direction, temperature, humidity and net-radiation data collated to hourly data. A rain-gauge, located in the uplands of each catchment provided additional rainfall data (to give a catchment average value). The weather data were used to predict soil moisture deficit (SMD) according to Schulte et al. (2005).

Soils with SMDs ≤0 mm are assumed to be able to transport available nutrients to water bodies in surface runoff and drainflow rapidly and, therefore, constitute high risk (Kerebel and Holden, 2013; Kerebel et al., 2013). Therefore, in order to identify critical times for nutrient mobilisation in the study catchments, the average time over the four study years that SMD ≤0 mm was determined on a weekly time scale for both well-drained and poorly-drained soils in each catchment. Both extremes of soil drainage capacity were used to capture the range of nutrient mobilisation risk in each catchment.

2.3. Field monitoring and analysis

Nutrients and sediments in water leaving each catchment were measured for four hydrological years (1st October 2010 to 30th September 2014) using a common experimental design. This consisted of sub-hourly, synchronous river monitoring of TP (0.000–5.000 mg l^{-1}, Table S2), TRP (0.000–5.000 mg l^{-1}, Table S2), TON (0.00–50.00 mg l^{-1}, Table S2) and turbidity (0–4000 NTU, Table S2) using bankside Hach-Lange equipment (Melland et al., 2012). In summary, TP and TRP were monitored using a Phosphax–Sigmatax suite of instruments that use a fully automated colorimetric analysis similar to the method described by Eisenreich et al. (1975), with the digestion procedure omitted on the TRP cycle. TON was measured using Nitratax SC-Plus UV instruments and was regarded as NO_3—N as previous work showed the nitrite-N fraction to be negligible (Melland et al., 2012). Similar equipment has been used and reported by Jordan et al. (2007, 2012) and Campbell et al. (2015) and which provide further details on the analytical methods and quality control. Routine (approximately monthly) grab sampling at sites coincident with the bankside analysis equipment

Table 1
Characteristics of the study catchments including the regular slurry closed period dates and derogations during the study period (October 2010–September 2014) to account for abnormal weather patterns. Annual rainfall is based on the hydrological years from 1st October 2009–30th September 2014.

	Size, km^2	Average annual rainfall, mm	2014 Average organic N & P loading, kg ha^{-1} yr^{-1}	Geology & aquifer	Regular closed period	Derogation 1: 2011 & 2012	Derogation 2: 2012	Derogation 3: 2013
Grassland A	7.5	1117	N: 168 P: 25	Devonian old red sandstone, mudstone and minor siltstone. Productive aquifer with a secondary permeability flow.	Oct 15th–Jan 12th	Oct 15st–Oct 31st	Nov 1st–Nov 16th	Jan 1st–Jan 12th
Grassland B	12.1	1078	N: 88 P: 13	Ordovician rhyolitic volcanics. Productive aquifer with faults.	Oct 15th–Jan 12th	Oct 15st–Oct 31st	Nov 1st–Nov 16th	Jan 1st–Jan 12th
Grassland C	3.5	1085	N: 85 P: 12	Silurian metasediments and organics. Unproductive aquifer except for local zones.	Oct 15th–Jan 31st	Oct 15st–Oct 31st	Nov 1st–Nov 16th	Jan 15th–Jan 31st
Arable A	11.3	1021	N: 34 P: 5	Ordovician-Silurian calcareous greywacke and banded mudstone. Poorly productive aquifer.	Oct 15th–Jan 12th	Oct 15st–Oct 31st	Nov 1st–Nov 16th	Jan 1st–Jan 12th
Arable B	9.4	913	N: 66 P: 10	Ordovician volcanic slate and silt stone. Poorly productive aquifer with fissure flow.	Oct 15th–Jan 15th	Oct 15st–Oct 31st	Nov 1st–Nov 16th	Jan 1st–Jan 15th

were collected and analysed in the laboratory for organic nutrient fractions (by subtraction) following filtration if necessary. These fractions were total N minus inorganic N to provide total organic N (Table S2), and total dissolved P minus dissolved reactive P to provide dissolved organic P (Table S2). Turbidity was rated to suspended sediment using samples of stream water suspended sediment (SS) concentrations, collected across discharge gradients, using SAS 9.3 (SAS Institute Inc., USA) (Sherriff et al., 2015). All catchments had OTT Orpheus-mini water level recorders adjacent to Corbett non-standard flat-v weirs. Water level was rated to discharge using OTT ADC and C31 flow meters (Mellander et al., 2014) and the WISKI 10-SKED rating curve editor.

Discharge, nutrient and sediment concentration records were stored in the WISKI 10 database management system for quality controlling, analysis and archiving. Daily 'event' discharges were quantified by applying a baseflow separation to hydrographs from the catchment outlets, using an established method (UK Institute of Hydrology, 1980). Storm events were defined as the top 90th percentile of ranked daily 'event' discharges (i.e. discharges that are elevated as a result of rainfall), representing a condition most likely to cause diffuse nutrient, including incidental, transfers (Campbell et al., 2015).

2.4. Critical times for nutrient delivery

Using the high-resolution datasets, loads of TP, TRP, TON and SS were calculated at 1 h intervals as the product of stream discharge ($m^3 h^{-1}$) and synchronous chemistry concentration ($mg l^{-1}$) (averages of 3–6 samples per hour), normalised to catchment areas. Weekly TP, TRP and TON loads were calculated for each catchment and study year, beginning on September 17th, i.e. four weeks prior to the beginning of the closed-period (October 15th). In order to separate the closed periods from the rest of the year, the loads during the days remaining in the last week of the closed period were collated as 'weekly' values. Similarly, the days remaining in the last week of the hydrological year were also collated as 'weekly' values.

2.5. Signals of increased nutrient source pressures

Evidence of increased nutrient source pressures were expected to be revealed as higher flow-weighted mean (FWM) nutrient concentrations in comparative storm discharges. Therefore, FWM TP, TRP and TON concentrations during storms were calculated as the quotient of daily TP, TRP and TON loads and daily discharge, for storm days (i.e. those with event discharges >90th percentile). Whilst some studies have observed NO_3—N losses in storm runoff following slurry applications (e.g. Ceretta et al., 2010), it was anticipated that N would be most observed as a groundwater signal which, in storm events, would be due to eventual flushing (Fenton et al., 2011).

The analysis was focussed towards the impacts of anticipated sudden practice change at the end of the closed period when organic nutrient application rates might be expected to increase rapidly and be available as incidental transfers. Therefore, additionally, and in order to more quantitatively assess if nutrient sources increased in runoff during the four weeks after the end of the closed period (i.e. the 'after' shoulder period), distributions of storm FWM TP and TRP concentrations were analysed for the four weeks prior to the end of (termed 'End'), and four weeks after (termed 'After'), the closed period, over the four study years. Pairwise comparisons of 'End' with 'After' were conducted using Mann-Whitney rank sum tests (Mann and Whitney, 1947) on the distributions. For this analysis it was assumed that 'End' likely represents residual losses only (any slurry applied before the closed period would likely to have been incorporated into the soil profile or lost in the autumn due to incidental runoff by this time) and other periods with significantly higher storm FWM TP or TRP concentrations may have experienced increased nutrient source pressures. A low storm frequency during the four weeks before the start of closed period (i.e. the 'before' shoulder period) precluded the capability and indeed the necessity for a similar analysis of this period. Organic nutrient fractions from routine grab samples were also extracted and compared if coincident with 90th percentile event flows.

2.6. Increased nutrient sources - disentangling residual and incidental nutrient signals

Elevated nutrient sources in similar storm discharges may indicate the presence of incidental slurry transfers; however, they may also indicate the presence of elevated residual nutrient transfers (for example from P-enriched soil). To disentangle this, and following Withers and Bailey (2003), this study used the available high resolution P data and specifically the TRP:TP ratio as incidental slurry P signal. Additionally, in the method reported by Bechmann and Vaje (2002), the TP:SS ratio at catchment outlets during storms was used. Both analyses were based on the expectation that elevated ratios (expressed as a percentage) during storms indicate the presence of a P source not associated with soil/sediment erosion dynamics, and potentially associated with incidental losses from slurry. Withers and Bailey (2003) did not identify a specific soluble to total P ratio threshold; however, Bechmann and Vaje (2002) attributed ratios of TP:SS <2% to soil erosion processes, i.e. part of residual transfer dynamics, but questioned the overall validity of this specific threshold. In this study, both ratios were used as a guide to identify stepped changes in storm hydrochemistry that might be indicative of slurry P pulses, rather than relying on threshold values to delineate pressures. A large storm dataset was necessary for this analysis to ensure that any data observed with high TRP:TP or TP:SS ratios were accepted as part of a runoff process trend and not outliers or 'noise' (Harris and Heathwaite, 2005).

3. Results

3.1. Critical times for nutrient mobilisation

From weeks 2–3 of the closed period until the end of February, the nutrient mobilisation risk was high (represented by SMDs ≤0 mm) nearly all of the time (for at least 96% of time within any one week) on the poorly-drained soils in four of the five catchments (Fig. 2) (except in Grassland A). However, on the well-drained soils in these catchments, there were some weeks during this period when the nutrient mobilisation risk was high for just ca. 20% of the week (Fig. 2), up to a maximum of ca. 80% of the week. Soil moisture conditions were more favourable in the free-draining Grassland A catchment during this period with a high nutrient mobilisation risk occurring between 75 and 100% of the time within any one week on the poorly drained soils and between 25 and 68% of the time within any one week on well-drained soils.

3.2. Critical times for nutrient delivery

On average over the four study years and five catchments, 0.76 kg TP ha^{-1} yr^{-1} (0.28–1.17 kg TP ha^{-1} yr^{-1} across catchments), and 23.2 kg TON ha^{-1} yr^{-1} (9.6–34.8 kg TON ha^{-1} yr^{-1} across catchments) was delivered to the catchment outlets (Fig. 3). Forty three percent (33–54% across catchments), and 45% (36–56% across catchments) of TP and TON loads, respectively, were exported during the 3 month closed period for slurry spreading, despite this period comprising just ca. 25% of the time within the year. Despite the disproportionately high nutrient loads during the closed period, the majority of loads occurred during the rest of the year (57% and 55% of TP and TON losses, respectively). Nutrient losses persisted throughout the spring months in most years and, in 2012, were particularly high during the summer months (Fig. 3). Total reactive P loads were approximately 50% of TP loads and mirrored trends in TP loads (see Supplementary Information, Fig. S2).

3.3. Signals of increased nutrient source pressures

The majority of storm discharges were <10 mm, with medians ranging from 2.73–6.19 mm (Fig. S3a). The associated median FWM TP TRP and TON concentrations ranged from 0.04–0.27 mgl^{-1}, 0.02–0.12 mgl^{-1} and 1.67–7.29 mgl^{-1} respectively (Fig. S3b–d). Based on the expectation that elevated nutrient source pressures are revealed as higher flow-weighted mean (FWM) nutrient concentrations during 'storms', TP, TRP and TON sources became elevated during all seasons, rather than during any particular season (Fig. 4a, b, c). The only trends of note were; i) an early autumn peak and subsequent decline in storm FWM TP, TRP and TON concentrations in the two poorly-drained catchments, which coincided with the beginning of the closed period and ii) a late winter peak in storm FWM TON concentrations in the well-drained Grassland A catchment.

A few storms in the 'before' (i.e. the four weeks immediately before the closed period), and 'after' shoulder periods (i.e. the four weeks immediately after the closed period) had elevated FWM TP (and occasionally elevated TRP) concentrations indicating the presence of elevated P sources (examples circled in Grassland A, C and Arable A, Fig. 4a). However, rank sum comparisons of storm FWM TP and TRP concentrations between the 'after' shoulder period and the preceding four weeks at the end of closed period (assumed to represent residual losses only) for four of the five catchments (Fig. 5) revealed similar median P concentrations between these periods ($P > 0.05$) for all catchments except Grassland C. These findings indicate that P source pressures did not significantly increase during the four weeks immediately after the closed period in the majority of catchments. Although storm FWM TP and TRP concentrations significantly increased after the closed period in Grassland C, median and mean storm FWM P concentrations during these four weeks were low and below the national environmental quality standard of 0.035 mgl^{-1} TRP.

Of significance were FWM TP and TRP concentrations during the spring and summer storms, when these occurred, which frequently

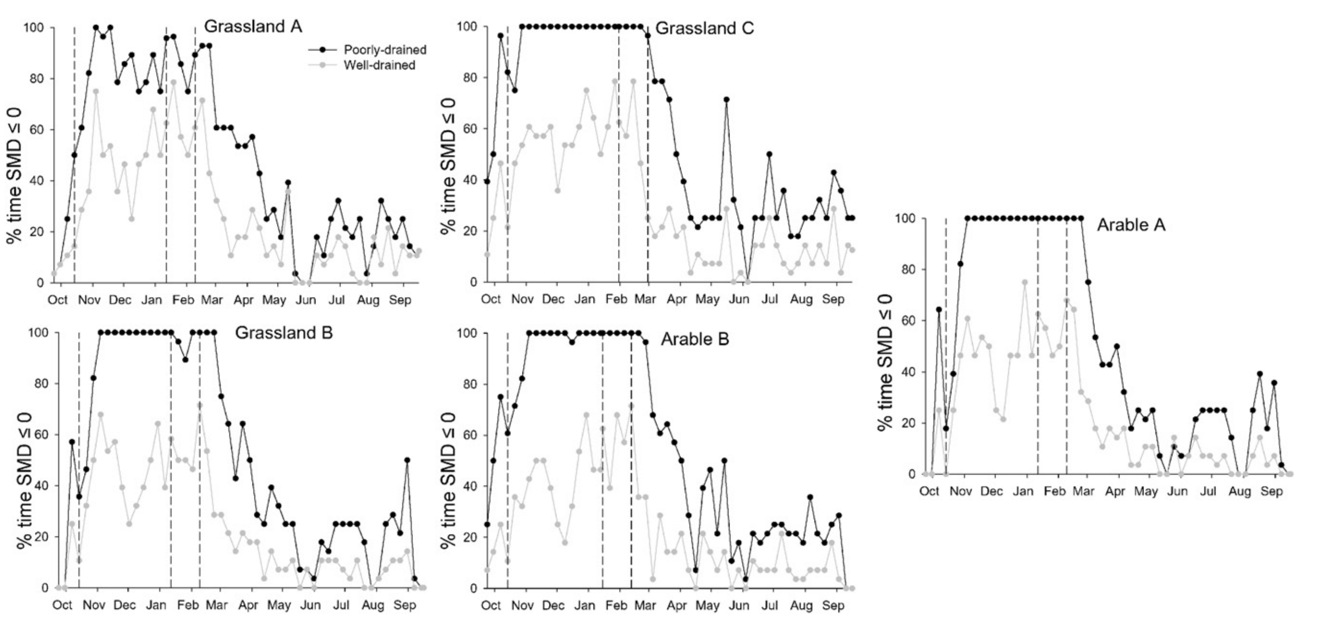

Fig. 2. Weekly, the average time over four years, that SMDs were ≤0, (assumed to represent critical times for nutrient mobilisation) in each study catchment for both well and poorly drained soil drainage scenarios. Black vertical lines represent the regular closed-period beginning and end dates as well as the adjacent four weeks prior to the beginning and after the end. In order to separate the open and closed periods, the days remaining in the last week of the closed period and the days remaining in the last week of the hydrological year were collated as 'weekly' values.

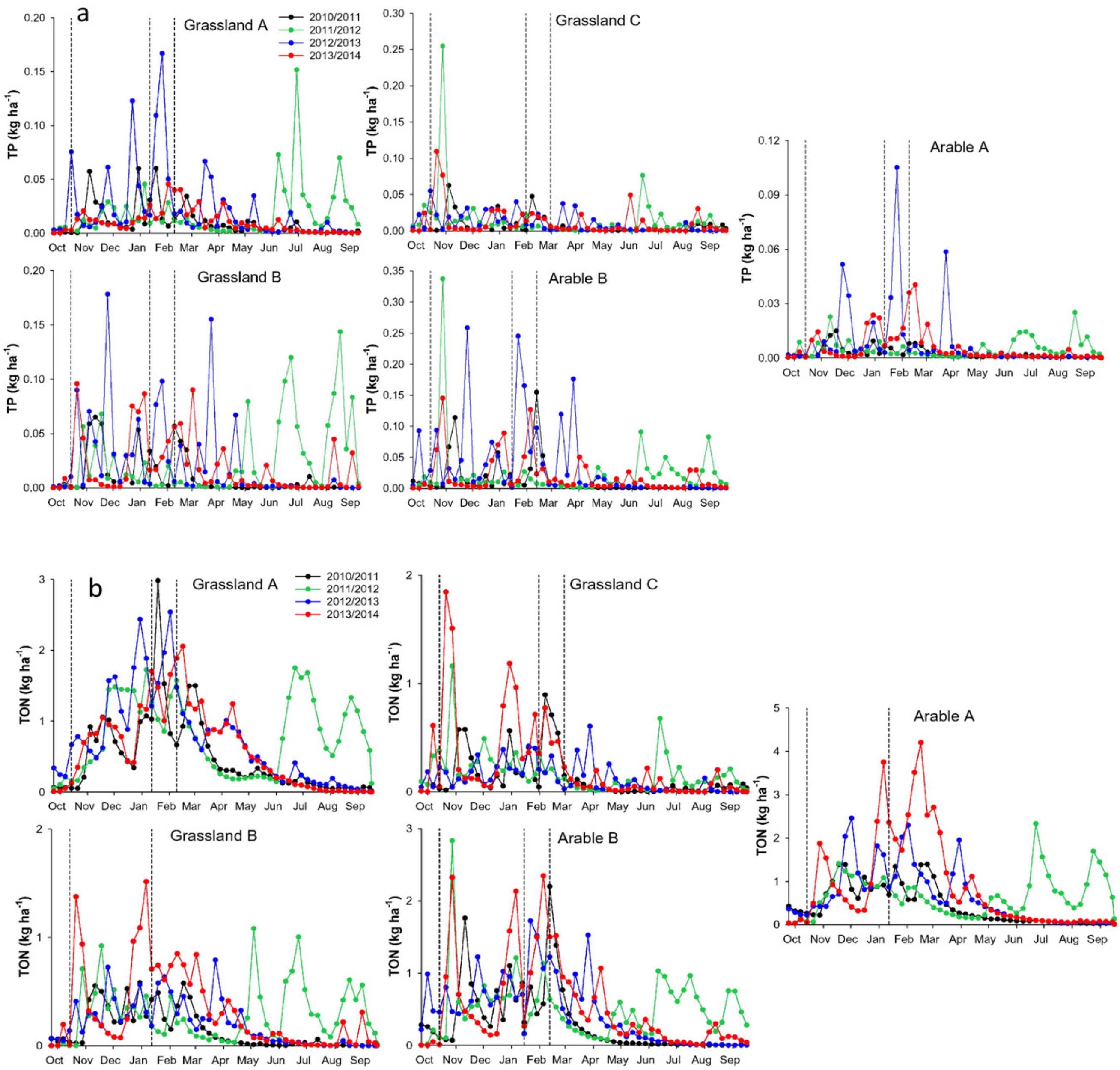

Fig. 3. Weekly loads of a) TP and b) TON over four years (October 2010–2014). Black vertical lines represent the regular closed-period beginning and end dates as well as well as the adjacent four weeks prior to the beginning and after the end. In order to separate the open and closed periods, the days remaining in the last week of the closed period were collated as 'weekly' values and the days remaining in the last week of the hydrological year were also collated as 'weekly' values.

indicated the presence of elevated P source pressures in all catchments. Storm FWM TON concentrations indicated the presence of elevated N source pressures during the summer in Grassland A (up to 7.35 mg TON l^{-1} in June 2012) and Grassland B (up to 5.61 mg TON l^{-1} in May 2012).

3.4. Increased nutrient sources - disentangling residual and incidental nutrient signals

Most of the high storm FWM nutrient concentrations did not coincide with high TRP:TP (Fig. S4) and TP:SS (Fig. 6) ratios as might be expected with stepped pulse changes associated with incidental transfer processes. However, the TRP:TP ratios did not systematically indicate any major stepped change in many storm events. This may be due to P reactivity in the particulate (colloidal) part of the TRP (unfiltered) fraction, as reported by Haygarth et al. (1997) and so not a clear signal of slurry P as with the filtered, soluble fraction (Withers and Bailey, 2003). The rest of the analysis was, therefore, restricted to TP:SS ratios.

High TP:SS ratios in 90th percentile storm events in the early closed period (October, November) in Grassland A (up to 9%), are possibly indicative of incidental P transfers following late Autumn slurry applications The consistently low TP:SS ratios in Arable A during the same storms, where organic P loadings are very small overall (Table 1), provides a strong validation for the use of this metric as a marker for organic incidental P transfers. Based on this, it appears likely that incidental losses also occurred during one storm at the beginning of the closed period in Grassland C (2011 – circled in Fig. 4a) and a three-week long storm before end of the closed period in 2014 in the same catchment. However, despite these ratios showing an overall stepped increase during these periods, the corresponding FWM concentrations were low in both Grassland A and C catchments.

With the exception of one storm in Arable B in January 2013, TP:SS ratios were low during both shoulder periods. These low ratios suggest

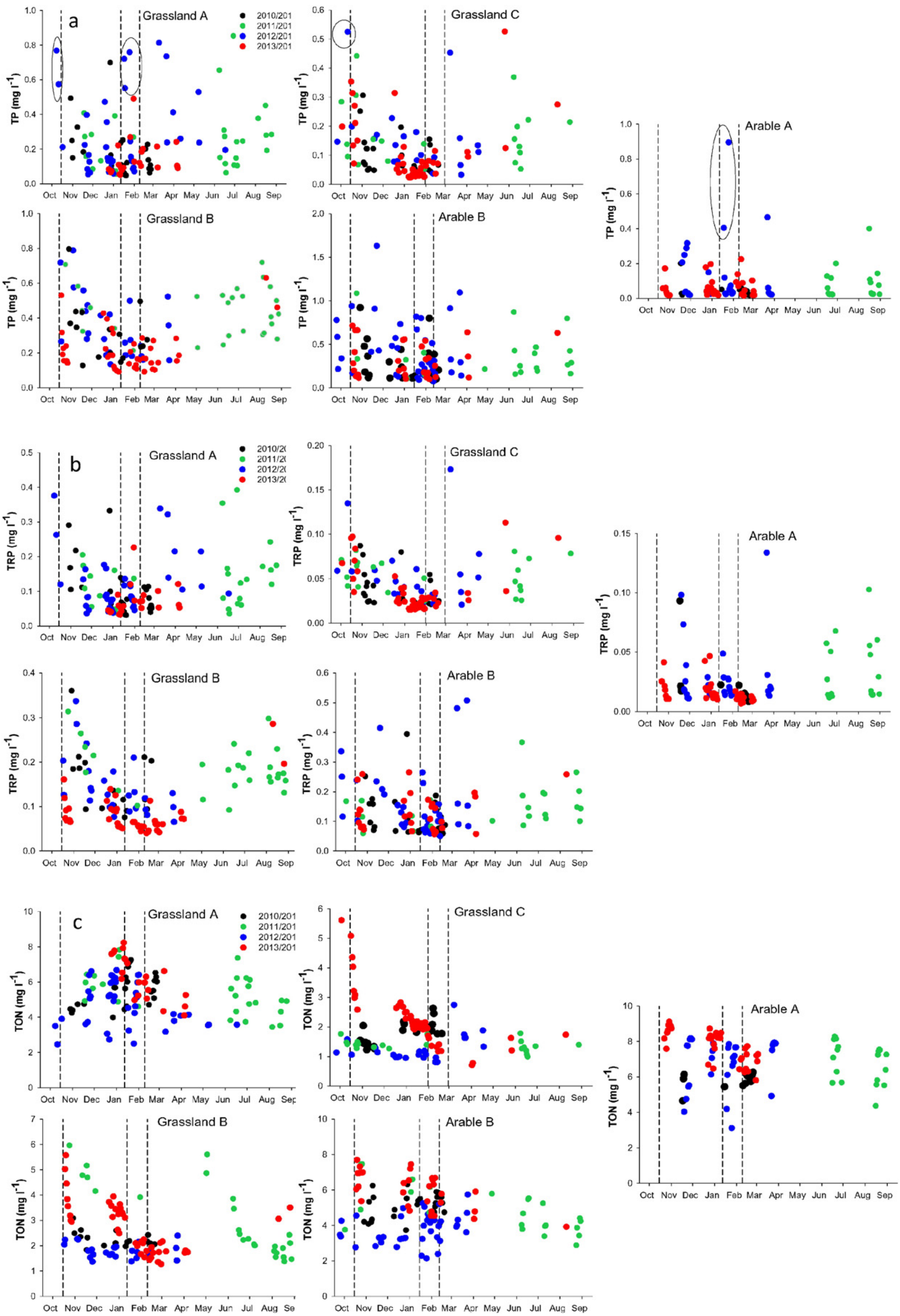

Fig. 4. Flow-weighted mean a) TP b) TON concentrations during 'storms' (upper 90th percentile of event flows) over four years (October 2010–2014). Black vertical lines represent the regular closed-period beginning and end dates as well as the adjacent four weeks prior to the beginning and after the end.

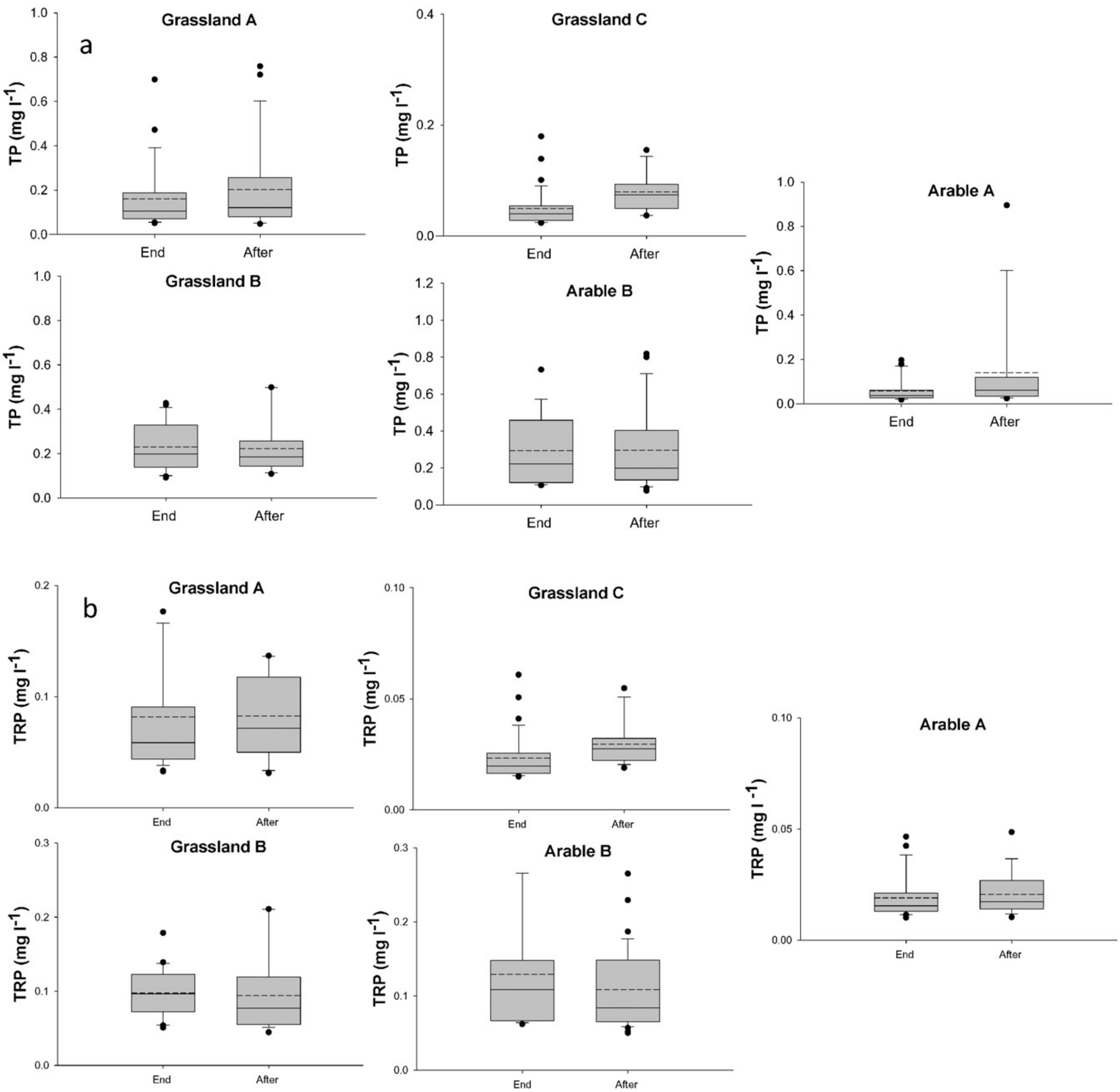

Fig. 5. Storm FWM TP concentrations for the four week periods at the end of (End) and after (After), the regular closed period, for four years (October 2010–2014).

that the P sources during these times were likely mostly derived from residual soil/sediment stores. The one storm in Arable B with much elevated TP:SS ratios (4%) also had elevated FWM TP concentrations (0.67 mg TP l^{-1}) which, when combined, are more indicative of incidental transfers.

The high FWM nutrient concentrations source pressures during the spring and summer storms in all catchments were mostly coincident with low TP:SS ratios, reflective of residual transfers. However in 2012, many of the summer storms associated with high FWM concentrations in Grassland A (June–August) and Grassland B (June) were associated with elevated TP:SS ratios indicating the presence of incidental P transfers during these storms.

Grab sampled organic nutrient fractions for Grassland A (well-drained) and Grassland B (poorly-drained) are shown in Table S1. The table shows the range of TP:SS data used in the daily event calculations (based on 10-min time-step) as well as the instantaneous TP:SS data coincident with the grab samples. The organic nutrient fractions offer no extra insight into residual and/or incidental nutrient transfers, likely because they are representing just one point in time during rapidly changing storm conditions. The large range in instantaneous TP:SS values during the storms highlights the dynamic nature of the conditions during which the grab samples were taken. The results do, nevertheless, show that validation of the parameters used here with either organic nutrients or one or more of the emerging tracing tools will need to be focussed on a similarly rich storm dataset.

4. Discussion

Many environmental mitigation measures are subject to review following an evaluation period based on impact monitoring (Reichenberger et al., 2007; Sharpley et al., 2009; Stewart et al., 2009). Specifically in the EU and regarding water quality, the overarching WFD legislation reviews data on water quality impact (status) from a range of pressures, including those from agricultural sources which

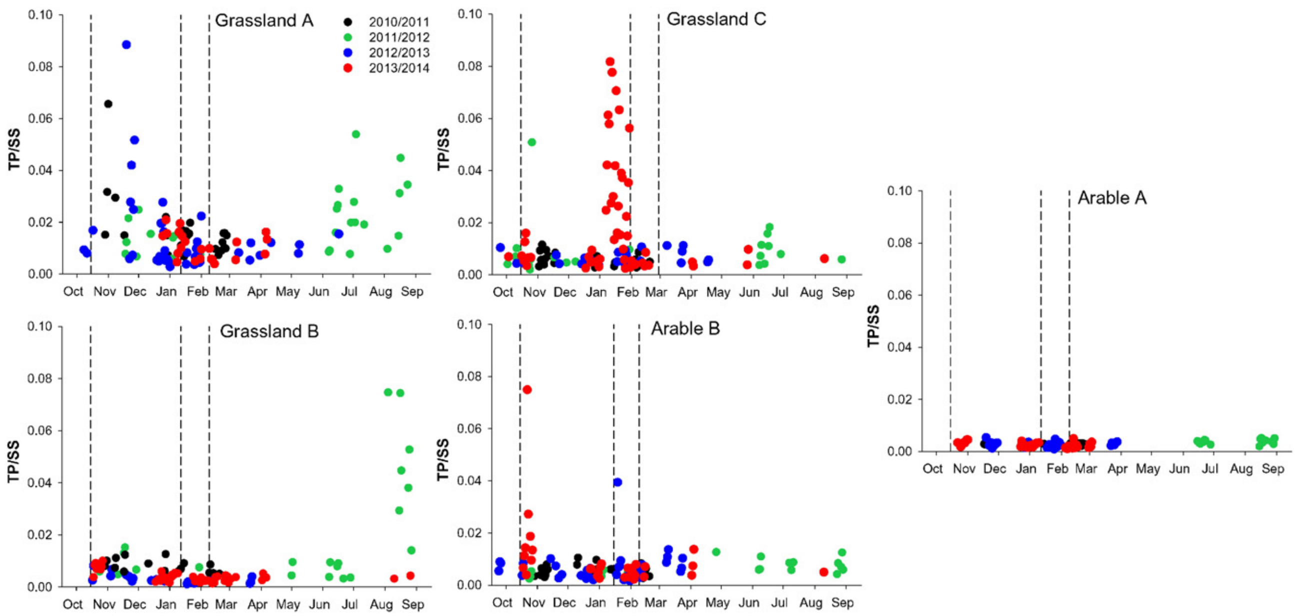

Fig. 6. Ratio of TP load to suspended sediment (SS) load during 'storms' (upper 90th percentile of event flows) over four years (October 2010–2014). Black vertical lines represent the regular closed-period beginning and end dates as well as the adjacent four weeks prior to the beginning and after the end.

are mitigated under the Nitrates Directive (OJEC, 1991). As the WFD enters a second cycle and targets for improved or maintained status are made according to prior monitoring data, it will be essential that those data are fit for purpose as admissible evidence in the review process (e.g. Harris and Heathwaite, 2005). With diffuse pollution processes, such as incidental nutrient transfers, an understanding and appraisal of cause and effect patterns of storm induced nutrient transfers is crucial. Whilst the results in this study are at most relevant for north-west European Atlantic pedo-climatic conditions, the framework of analysis is applicable more universally.

4.1. Closed period

The disproportionately high nutrient losses during the closed period were reflective of the soil hydrological conditions, which were often saturated (as indicated by the SMD model), rather than the status of nutrient source pressures during this time. This pattern is supported by previous studies in these catchments (Jordan et al., 2012; Shore et al., 2014; Mellander et al., 2015) and elsewhere (Buda et al., 2009; Dupas et al., 2015), which have documented the dominance of climatic and soil hydrology controls, rather than P source controls (e.g. soil P, organic P loading) on P losses in agricultural catchments. Nevertheless, any increased source pressures would exacerbate existing losses and should be identified and managed where possible. The autumn flushes in the poorly-drained catchments appear to be controlled by residual transfer processes which could include processes of soil microbial cell lysis (Blackwell and Brookes, 2010; Turner and Haygarth, 2001) and soluble P flushes following protracted dry spells (Dupas et al., 2015; Kurz et al., 2005), and/or stream bed/bank sediment erosion (Sherriff et al., 2015), all of which would be difficult to attenuate.

Whilst the 'autumn flush' was not apparent in Grassland A, elevated FWM TP and TRP concentrations occurred at random during some of the autumn storms. The presence of high TP:SS ratios during some of these storms in October and November suggests that incidental P transfers may have occurred during this time. This is further supported by slurry application data recorded in this catchment by Murphy et al. (2015a). In this study, most slurry applications occurred during the spring and summer growing period to best utilise available nutrients. However, an increase from approximately 5% of total annual P applied in organic fertilisers in September to approximately 15% of total annual P applied in the first two weeks of October (for example, in 2010) was recorded. This effective loading of nutrients prior to the onset of the closed period could reflect an effort to empty tanks prior to winter housing of animals whilst the land is still trafficable. This early autumn application may still be available to storm runoff later in the autumn hence the random occurrence of elevated FWM P concentrations and high TP:SS ratios during this time. Reducing these incidental source pressures in autumn should be considered along with reducing the residual source pressure associated with autumn flushes on poorly-drained soils.

The patterns of storm TON delivery in Grassland A, peaking in late January, are likely reflecting N sources that were mobilised during the preceding autumn storms and were slowly flushed in sub-surface pathways following leaching and transformations. This lag time estimate of 4–5 months corresponds with similar lags of flushing to deeper groundwaters found in a separate study in this catchment (Mellander et al., 2014). However, the data are not clearly showing whether this peak following the lag is associated with late autumn slurry application nitrifying to NO_3 and leaching or from other mineralised N leached from residual N stores between the autumn and winter. The absence of such lag-effects in freely-draining Arable A are not surprising given the highly permeable nature of the bedrock in this catchment which facilitates faster travel times for flow and associated pollutants, compared to Grassland A (Mellander et al., 2014, 2016).

The theory that slurry transfers could become diluted at catchment scales with a low overall impact on P delivery has been suggested by Haygarth et al. (2012) and may be a feature of the closed period in Grassland C, where high TP:SS ratios correlated with low FWM TP and TRP concentrations at the beginning (one storm in 2011), but mostly at the end (3 week storm in 2014), of the closed period. However, the reason for this apparent incidental transfer was not clear but the risk associated with a particularly long period of storm runoff could have mobilised some sources not ordinarily connected – in yards, for example, and was sufficiently diluted.

4.2. Shoulder periods

The two shoulder periods differed greatly in their potential risk to downstream water-bodies, with the 'after' shoulder period (4 weeks after end of closed period) exporting much higher nutrient loads than the 'before' shoulder period (4 weeks before start of closed period).

The higher nutrient loads in the 'after' shoulder period reflected the soil conditions (which were relatively wet – see Fig. 2) rather than the nutrient source pressures (which were not particularly elevated – Figs. 4, 5) during this time. That is to say, there appeared to be very little evidence of incidental nutrient transfers (as indicated by low storm FWM concentrations and TP:SS ratios) during this time, apart from the storm in Arable B in 2013 (with elevated storm FWM concentrations and TP/SS ratios). Two possible scenarios could explain a low incidental transfer risk during this time. Firstly that spreading at these vulnerable times did not occur; this is likely in situations where lower animal intensities mean that slurry production is low and can be spread when trafficability is more suited, as found in a study of farmer attitudes and behaviour by Kerebel et al. (2013). This scenario is likely on poorer drained soils that preclude both animal intensity and early trafficking. Secondly, if spreading did occur, then it is likely to have occurred on the more freely draining soils which support both higher stock intensities and earlier trafficking. Whilst further behavioural data would be needed to support these assertions, as an example, Murphy et al. (2015a) found that February, including the four week period in the current shoulder analysis, was a known period for slurry spreading in the Grassland A catchment – a catchment of higher organic nutrient loading (hence a requirement to empty stores and provide early nutrients for grass growth) and with free draining soils to facilitate trafficking.

4.3. Open period

The data presented here showed a distinct storm nutrient loss risk during the spring/summer time, with evidence of increased source pressures (high FWM P and N concentrations), attributed to both residual and incidental transfers. The transient nature of incidental P sources may provide better opportunities for targeted management during these particularly risky times than the more continuous residual P sources. Whilst the incidental transfers were only evident in 2012 when conditions were unseasonably wet, they are a concern considering spring/summer is the period when the aquatic ecological risk is greatest in temperate climates (Boynton et al., 1996). Furthermore, summer storms may become more frequent in western Europe in coming years according to proposed sustained climate scenarios for the western Atlantic fringe (Semmler et al., 2008; Dunne et al., 2009). Summer storms can exacerbate existing wet soil conditions, with runoff occurring via saturation-excess overland flow (Dunne, 1978; Campbell et al., 2015) or occur as intense convective systems, whereby runoff is mainly via infiltration-excess overland flow (Horton, 1931; Doody et al., 2010). The former can be predicted more easily using SMD data thus may form a better focus point for management.

4.4. Policy implications

There has been a general improvement in agricultural nutrient use and water quality in water body types throughout the EU, and in Ireland where this study was undertaken (O'Dwyer et al., 2013; Ní Longphuirt et al., 2015; EPA, 2015; Buckley et al., 2015; EEA, 2015; Buckley et al., 2016). Policy reviews, therefore, need to be cognisant of these trends as well as increased process understanding of known pressures. From this study, five potential research and policy implications emerge.

1. The disproportionately high nutrient losses during the regulated closed period, proposed here as predominantly residual losses but also random early incidental losses from late applications (during the open period), support the notion of restricting nutrient applications during this time, as any additional source pressures may exacerbate the existing losses during a highly vulnerable period.
2. The data presented here, showing an occasional but distinct residual and incidental nutrient transfer risk during the spring/summer time due to the coincidence with unseasonal storm events (when the ecological risk is greatest), highlights the need for a more considered approach to spring/summer spreading.
3. However, consideration of spring/summer constraints to slurry spreading, also has to be balanced with the need to avoid concentrated applications prior to the closed period in preparation for housing of cattle and sheep, to avoid early peaks in storm P concentrations at the beginning of the closed period and, possibly, adding to subsequent peaks in FWM TON concentrations following a groundwater lag.
4. The findings in this study are related to an available high resolution dataset that considers storm nutrient hydrochemistry systematically throughout the year and facilitates statistical comparisons. For validation, the use of more sophisticated tracing techniques, including organic nutrient fractions, is required but will need to be based on a similarly rich, storm-focussed dataset.
5. At the least the behaviour of focussing applications, at those times (higher SMDs) and/or those places (more freely drained soils) when potential for nutrient mobilisation is low, should be particularly applied at the end of the open period (October), during derogated spreading periods and for summers characterised by wetter soil conditions. This apparent behaviour, in time and space, will need to be factored into the development of catchment water quality models that are based on rainfall-runoff processes and include surface water-groundwater interactions. This will be a particular challenge and with longer time series of isolated storm events could, for example, be interpreted using time series analysis.

Many nutrient mitigation programmes (Zhang et al., 2012; S1 31, 2014) restrict nutrient applications before and during stormy weather conditions and the data presented here highlights the need for renewed focus on this measure. Improved dissemination of fertiliser-application specific weather warnings to farmers, including the suitability of ground conditions for fertiliser application (e.g. short-term SMD forecasting), made widely available using more local meteorological forecasting and dissemination, may greatly support the awareness and successful implementation of this measure during open periods.

5. Conclusions

This study investigated high resolution nutrient concentration and river discharge data over four years and five catchments to investigate the seasonality of nutrient losses with emphasis on critical times of nutrient delivery relating to slurry open and closed spreading periods. An emphasis on seasonality and the magnitude of nutrients in storm discharges of similar magnitude was made possible by a higher-resolution dataset. The key findings were that:

- Over four years and five intensive agricultural catchments, average annual TP loads of 0.76 kg ha^{-1} (0.28–1.17 kg ha^{-1}) and TON loads of 23.2 kg ha^{-1} (9.6–34.8 kg ha^{-1}) were disproportionately high during the closed winter period (43% and 45%, respectively, during ca. 25% of the year), apparently delivered as residual losses with some early incidental losses from autumn slurry applications. However, these signals will require some other validation from one or more emerging hydro-biochemical tracing tools.
- Despite modelled soil moisture data indicating a continued vulnerability to nutrient mobilisation in the four weeks following the end of the closed period, there was no clear evidence of systematic incidental transfers during this shoulder period, as indicated by low storm FWM TP concentrations and TP:SS ratios. This infers that slurry either wasn't spread during these four weeks (and subsequently lost as incidental transfers in storms), that slurry was spread on more freely draining soils where the risk of mobilisation was low, or was excessively diluted.
- The data in this study showed a distinct storm nutrient loss risk during the spring/summer time, with evidence of increased source pressures (high storm FWM P and N concentrations), attributed to both residual

and incidental transfers. This is a concern considering this is the period when the ecological risk is greatest.

- The apparent behaviours from the beginning of the open period, that is likely to be focussing slurry applications at those times (higher SMDs) and/or those places (freer-draining soils) when potential for nutrient mobilisation is low, could be disseminated further. This would help to diminish the incidental mobilisation risk associated with late autumn applications, derogated periods and also, more importantly, help to diminish the risk associated with storm driven incidental nutrient transfers during sensitive summer periods.

These findings progress the knowledge of storm driven incidental nutrient transfers in agricultural catchments, and point to a knowledge transfer augmentation of conditions relating to the best time and best place for applications during open periods, within an existing EU regulatory framework of closed periods. For policy review purposes, the findings show that the interpretation of higher resolution data is quite crucial. Here, for example, capturing the nutrient, sediment and discharge dynamics of storm induced incidental and residual nutrient transfers provides an improved understanding of cause and effect, which can be augmented as other data become available at high resolution.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.02.085.

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